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# The Metallurgist.

*Supplement to* The Engineer, *June, 1937.*

## Lead Bronzes.

THE organisation of the national economy in Germany is having its effects in all branches of technical activity in that country, and references to it are now frequent in metallurgical publications. Special importance is attached to the conservation of tin and copper, and to the English reader it is an unfamiliar experience to find this consideration receiving close attention in an article on lead bronzes.* In studying this and similar communications in German technical literature it is necessary to bear in mind these special circumstances, since considerations which have force in Germany do not necessarily apply in countries where the State does not place restrictions on access to particular metals.

The mechanical properties of a wide range of lead bronzes are tabulated below in the form of a suggested specification, but the author points out that these in themselves give no indication of the bearing properties of the various alloys, although they may be of interest for checking the quality of massive castings. The same table gives an indication of the most suitable lead bronzes for different applications, and in the case of bearings it is necessary to consider, in addition to alloy compositions, two distinct types of construction. These are the solid bearings, on the one hand, and on the other, the bi-metal or "cast on" bearings, in which a relatively thin layer of lead bronze is joined by alloying to a shell of stronger material, usually steel.

### SOLID BEARINGS.

Solid bearings of lead bronze may vary from a pound or two up to a ton in weight; the service to be expected from them is known, and years of experience have confirmed the suitability of lead bronzes for the largest types of bearing.

The consumption of non-ferrous metals is only affected to a limited degree by a simple substitution of lead bronze for tin bronze and gun-metal in solid bearings without changing the dimensions. Even such small saving as is achieved in this way is likely to be outweighed by losses due to the greater difficulty of making lead bronze castings, and the necessity, in the case of large bearings, of taking special measures, as, for example, the addition of nickel, to prevent segregation.

If the substitution of lead bronze for tin bronzes and gun-metals can be accompanied by a reconsideration of design, however, substantial economies can be effected, since advantage can then be taken of the remarkable load-carrying capacity of lead bronze as a bearing material. This generally permits a reduction of the length of the bearing, and, in consequence, a saving of 25 to 30 per cent. in the metal required. An example is quoted in which one engineering works was able in this way to replace gun-metal bearings having the composition copper 85 per cent., tin 9 per cent., zinc 6 per cent., and totalling 6000 kilos. in weight by only 2000 kilos. of lead bronze bearings.

An interesting sidelight on the extent to which the conservation of copper and tin has progressed in Germany is provided by figures quoted for the non-ferrous metal components of a locomotive on the State Railways. In the example taken these amounted formerly to 8090 kilos., and have now been reduced to 628 kilos. Metallic copper in the form of fire-boxes, &c., has fallen from 5000 kilos. to 50 kilos., gun-metal (copper 85 per cent., tin 5 per cent., zinc 7 per cent., lead 3 per cent.) from 2900 kilos. to 530 kilos., and whitemetal (containing 80 per cent. tin) from 190 kilos. to 48 kilos. This case is used to demonstrate how a still greater economy could be achieved by the use of lead bronze in place of the gun-metal; 500 kilos. of this gun-metal contains 425 kilos. copper, 25 kilos. tin, 35 kilos. zinc, and 15 kilos. lead, and this would be replaced by 440 kilos. lead bronze, evidently containing approximately 20 per cent. lead. This would save 75 kilos. copper, 25 kilos. tin, and 35 kilos. zinc, with an extra requirement of 75 kilos. lead. The monetary saving on each locomotive with copper at 0·50 RM per kilogramme (say, £42 per ton), and tin at 3·30 RM per kilogramme (£275 per ton) would be 118·00 RM, or, in round figures (with 12 RM to the £) £10 sterling.

### BI-METAL (BRONZE-LINED) BEARINGS.

In this type of bearing the lead bronze is supported by the shell of steel to which it is bonded. Since the thickness of the lining is generally about 0·50 mm. to 0·75 mm., the bronze required is only a very small fraction of that used in a solid bronze bearing, so that the advantages of lead bronze, from the point of view of economising in the use of non-ferrous metals, are realised to a much greater degree with bi-metal bearings than with the solid bearings.

These considerations go to strengthen the case for bronze-lined bearings, already strong on the purely technical grounds of their remarkable load-carrying capacity and their running properties. Satisfactory performance has been given by such bearings with pressures up to 350 kilos. per square centimetre (approximately 5000 lb. per square inch) and running speeds of 10 m. per second (33ft. per second) at 20,000 r.p.m.

The high lead contents—up to 40 per cent.—which can be employed in steel-backed bronze linings give a considerable margin of safety in the event of a

* Willi Claus, "Zur Frage der Blei-Bronzen," *Metallwirtschaft*, January 29th, 1937, pages 109–114.

failure of lubrication. An example is given of a bearing bush 48 mm. diameter and 48 mm. long running under a pressure of 100 kilos. per square centimetre. On shutting off the oil supply the shaft continued to turn for several minutes before being brought to a standstill. On examination it was found that no true seizure had occurred, the heat developed having caused a film of lead to sweat out on the surface of the bush. On repolishing the bore of the bush the bearing ran quite smoothly again with normal lubrication. A similar experience is described in connection with a large compressor where there was a failure of oil—it is remarked that with any bearing material other than lead bronze serious damage must have resulted.

As an illustration of the saving in non-ferrous metals it is reported that in a particular grinding spindle a weight of 0·15 kilos. of lead bronze in the form of a lining in a steel shell sufficed to replace a solid tin bronze bush containing 14 per cent. tin and weighing 14 kilos.

In the manufacture and application of bi-metal lead-bronze bearings attention has to be paid to certain considerations which do not come into account, or are of minor importance, with solid bearings.

In the first place, the process of manufacture must ensure a perfect and continuous metallic union between the bronze lining and the steel shell. The success of the process in this respect can be judged by microscopic examination of polished sections through the junction and also by bending tests—the lining should not part from the shell even when a duplex strip cut from the bearing is bent double, with the bronze in tension.

The methods used in the final machining of lead-bronze-lined bearings are governed by the fact that lead bronze does not "run itself in" in the same way as whitemetal; a lead-bronze lining is not scraped to fit, therefore, but must be finished by fine boring, preferably with a diamond tool.

It is partly for the same reason that the clearance, with simple lubrication, must be larger with lead bronze than with whitemetal bearings. The specific friction between lead bronze and oil is relatively high, and this also demands a fairly generous clearance. Normal practice in engine bearings is to use a clearance of 1/1000 to 1·5/1000 of the journal diameter.

A decision as to the correct clearance to be adopted can be arrived at generally only by a separate consideration of individual cases. Thus, it is necessary to distinguish between the conditions in a light Diesel engine, with high dynamic loading and

*Lead Bronzes.*

| Group. | Identification. | Approximate composition, per cent. | | | | | | Mechanical properties. | | | Applications. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cu. | Pb. | Sn. | Zn. | Ni. | Special elements. | Tensile strength, kg./sq. mm. | Elongation, per cent. | Brinell hardness. | |
| | Lead bronze I | 97 | <3 | — | — | — | — | 15–20 | 40–15 | 25–50 | Castings for severe thermal and electrical duty, *e.g.*, blast-furnace tuyères, hot blast valves, collector brushes. |
| Lead bronzes | Lead bronze II | 97–60 | 3–38 | — | — | 0–3 | Up to 1% S in place of, or with nickel | 8–12 | 4–8 | 28–35 | Bi-metal bearings with steel shells; main and connecting-rod bearings for high-speed combustion engines, turbine, locomotive, machine tool, pump bearings. |
| | Lead bronze III | 60 | 38 | — | — | 0–3 | | 8–10 | 4–6 | 25–30 | |
| Lead-tin bronzes and special bronzes. | Lead-tin bronze 4* | 86 | 4 | 10 | — | — | — | >18 | >15 | >70 | Solid bearings for hot rolling mills, electrical machines. Castings to withstand high pressures and for chemical industry. |
| | Lead-tin bronze 12* | 80 | 12 | 8 | — | — | — | >15 | >8 | >60 | Solid bearings, with high bearing pressures, *e.g.*, cold rolling mills. Pressure-tight castings, Castings for chemical work. |
| | Lead-tin bronze 22 | 68–70 | 15–25 | 4–7 | — | — | — | 15–18 | 6–10 | 60–70 | Solid bearings, *e.g.*, for piston pins in Diesel engines, bushes for aircraft wheels, electric motors, mill machinery, water pumps, railway carriages and wagons. Bi-metal bearings with shell of different metal. |
| | Special lead bronze 2 | 60–70 | 20–28 | 0–8 | 0–3 | 1–8 | Mn, Si, Sb, Mg, Al, P, &c., according to practice of manufacturer | 12–20 | 10–5 | 40–60 | Solid bearings for heavy duty. Bi-metal bearings, *e.g.*, for milling machines, turret lathes, grinding machines, and chemical industry. |

* Existing German Specification D.I.N.1705 covers tolerances in chemical composition of these bronzes.

relatively great deflections of shaft and crank case and those in machine tools. Among machine tools, again, there are two classes—one employed for fine machining with low static loads, and the other in which rough cuts cause strongly alternating stresses.

Where necessary, however, extremely small clearances can be used quite safely with lead-bronze bearings provided that the oil pressure is sufficiently great. Thus, in certain machine tools, diametrical clearances of 0·5/1000 to 0·75/1000 are possible with oil pressures of 4 to 6 atmospheres. The low coefficient of expansion of the steel shell in bi-metal bearings is advantageous in maintaining such small clearances uniform. Bearings of this type become almost indispensable for operations where the highest precision must be maintained, as in grinding spindles, lathes, milling machines, and certain types of rolling mill. In these cases whitemetals are unsatisfactory because of the development of excessive play in the bearings.

A complete examination of the economics of the bi-metal lead-bronze bearing must take into consideration the utilisation of worn-out bearings. Since every effort is made to work with as thin a lining as possible, the loss of bronze when a bearing is discarded is extremely small and is not to be compared with the loss of metal when old solid bearings are remelted. With the perfection of methods for recovering non-ferrous metals from tinned and plated steel there is a good prospect of similar processes being applied to the recovery of the bronze in the linings of old steel-backed bearings.

The cost of bi-metal bearings is inevitably greater than that of solid bearings. Even apart from the outlay on development and investigation the manufacture of bi-metal bearings is more specialised and requires more expert supervision than the straightforward foundry methods applicable to solid bearings. On the other hand, high first cost is outweighed by the longer life and the avoidance of refitting charges. The life of lead-bronze-lined bearings in explosion engines is five times as long, on the average, as that of whitemetal bearings. The lead-bronze bi-metal bearings in the engines of the airship "Hindenburg" completed 1600 hours of service without renewal.

As may be gathered from this report, the author is not lacking in enthusiasm for the merits of lead bronzes as bearing metals, especially in the steel-backed construction with thin linings. His main theme is the opportunity they give for reducing the consumption of non-ferrous metals in engineering construction; but in this country, while the capabilities of these bearings are fairly generally recognised, the financial aspect presents a more serious obstacle than appears to be admitted in the article under review. For example, it is true that when a bi-metal bearing is discarded the loss of bronze is negligible, but by far the greater proportion of the cost of such a bearing arises from the expense of fabrication, and none of this can be recovered from a scrapped bearing. It is only in rare cases that an old shell can be remetalled with bronze.

The author does not touch on the tendency of lead bronze to score the shaft as compared with whitemetals, nor on the necessity to use hardened steel for crank pins and journals. These, together with the relatively high first cost, are among the chief factors hindering the wider use of steel-backed lead-bronze bearings in England, and it is probably true to say that in this country such bearings are not used in a particular application until it has been demonstrated beyond doubt that whitemetal is incapable of giving the service required. This having been said, it must also be agreed that in these cases steel-backed lead-bronze bearings have been extremely successful. Road vehicle C.I. engines and certain aero-engines provide examples where this type of bearing has made all the difference between the failure and success of a design.

It is now possible to manufacture bi-metal lead-bronze bearings of high quality by several processes, and the failure in service of such bearings is very rare. The next important development which is required is the working out of methods which will enable the bearings to be produced at a substantially lower cost than at present. If progress can also be made on the metallurgical side in removing the limitations on the type of steel surface with which they can operate, a wide extension of the field of application of lead-bronze bearings can be anticipated.

## The Diffusion of Gases Through Metals.

THE "Proceedings" of the Royal Society* for May, 1936, contains a paper from the Research Laboratories of the General Electric Company, W mbley, in which Dr. C. J. Smithells and Mr. C. E. Ransley describe some further work on the diffusion of gases through metals. The work is divided into three sections:—(1) The degassing of commercial nickel; (2) the diffusion of carbon monoxide through nickel; and (3) the diffusion of carbon and of oxygen through nickel.

### THE DEGASSING OF NICKEL.

The method adopted was to heat the metal, in the form of a coil of wire, suspended by fine tungsten wires in a lamp bulb. High-frequency heating was employed. The gas extracted was chiefly carbon monoxide with some carbon dioxide, hydrogen, and some small quantities of water vapour. A certain amount of surface gas probably derived from impurities worked into the surface during manufacture was also detected. This gas could be removed by heating the metal for 5–10 minutes in a vacuum or pure hydrogen, treatment which failed to remove any appreciable quantity of gas from the body of the metal. The quantity and nature of the gas removed as the temperature was progressively increased is given in Table I:—

TABLE I.—*Evolution of Gas at Different Temperatures from 1 mm. diameter Wire.*

| Time of heating. | Temp., deg. C. | Gas, cu. mm./gm. | | | Total. |
|---|---|---|---|---|---|
| | | $CO_2$. | $H_2$. | CO. | |
| 20 min. ... ... | 750 | 0·8 | 2·3 | 3·6 | 6·7 |
| 20 ,, ... ... | 850 | 0·3 | 0·3 | 3·3 | 3·9 |
| 20 ,, ... ... | 950 | 0·3 | 0·3 | 5·4 | 6·0 |
| 20 ,, ... ... | 1050 | 0·5 | 0·3 | 4·5 | 5·3 |
| 20 ,, ... ... | 1150 | 0·3 | 1·1 | 1·3 | 2·7 |
| | | | | | 24·6 |

The effect of the thickness of the wire was also investigated. The rate of degassing in hydrogen at 950 deg. Cent. is shown in Table II.

Periods of surface exposure (24 days) did not appear

* 1936, A, 155, 195.

to lead to an increase in the amount of gas which could be extracted, but deliberate oxidation of the surface resulted in a quite definite increase in the gas content.

TABLE II.—*Effect of Wire Diameter on Rate of Degassing in Hydrogen at 950 deg. Cent.*

| Time of treatment. | Residual gas in cu. mm./gm. 6 mm. dia. | 1 mm. dia. |
|---|---|---|
| 15 min ... ... | 15·1 ... ... ... | 12·6 |
| 2 hours ... ... | 13·8 ... ... ... | 5·1 |
| 6 ,, ... ... | 10·3 ... ... ... | 2·0 |
| 7½ ,, ... ... | 9·8 ... ... ... | 1·6 |

In a discussion of these results it is shown that Fick's linear diffusion law leads to the expression

$$\log q = \frac{\log 2\,C\,\Delta}{r} - 5\cdot 8\,\frac{\Delta\,t}{r^2}$$

where $q$ is the rate of evolution of gas from the wire, C the initial concentration of gas in the metal (c.c. at N.T.P. in 1 cubic centimetre of metal), $r$ is the radius of the wire in centimetres, $t$ is the time of degassing in seconds, and $\Delta$ the diffusivity constant of the gas in the metal.

If, for the degassing of a particular wire at a constant temperature, $\Delta$ remains constant we have for high values of $t$

$$\log q = A - B\,t.$$

The logarithm of the rate of gas evolution plotted against time should give a straight line and the change of slope of this line with temperature will be directly proportional to the variation of the diffusivity constant with temperature. The degassing of a wire at 950 deg. and 1050 deg. Cent. was determined with liquid air in a trap connected with the apparatus, and the palladium tube heated continuously. Assuming the nitrogen content to be negligible, the evolution of CO only was determined. If the rate was plotted logarithmically against time a graph was obtained which was linear after two hours (950 deg.) and after 40 minutes (1050 deg.). The temperature coefficient of the diffusivity constant, determined from these two slopes, was 3·6.

## THE DIFFUSION OF CARBON MONOXIDE THROUGH NICKEL.

Measurements were made at 900 deg. Cent. of the diffusion of carbon monoxide through nickel tubes using the apparatus previously described.† These measurements were, however, complicated by the fact that the gas is decomposed to some extent by the metal. Two experiments gave :—

| Pressure, mm. | Temp., deg. Cent. | Rate D. c.c./sec./sq. cm. for 1 mm. thick. |
|---|---|---|
| 235 ... ... ... | 900 ... ... ... | $3\times10^{-9}$ |
| 160 ... ... ... | 900 ... ... ... | $2\cdot7\times10^{-9}$ |

This rate is quite insufficient to account for the rate at which carbon monoxide can be extracted from nickel and the authors come to the important conclusion that the gas cannot be present in the metal as carbon monoxide, but is derived from a reaction between dissolved oxygen and carbon probably present as nickel oxide and nickel carbide.

## THE DIFFUSION OF CARBON AND OXYGEN THROUGH NICKEL.

This was accomplished in a very ingenious manner. It was not found possible to prepare nickel containing exact amounts of oxide and carbide, so carbon was deposited (by passing hydrogen containing 2 per cent. of acetylene through the heated tube) in the inside of the tube which was then mounted in the diffusion apparatus and sufficient oxygen admitted to keep the surface of the bulb in an oxidised condition. Under these conditions it was found that, on heating the tube in the usual way, carbon monoxide was produced inside the tube and carbon dioxide at the outside (oxidised) surface. By measuring the rate of evolution of these gases the rate of diffusion of oxygen and carbon in opposite directions through the wall could be determined. Some results are shown in Table III :—

TABLE III.—*The Diffusion of Oxygen and Carbon Through Nickel. Oxygen Pressure, 3·77 mm.*

| Temp., deg. Cent. | Rate of CO evolution, c.c./sec./sq. cm. for 1 mm. thick. | Rate of $CO_2$ evolution, c.c./sec./sq. cm. for 1 mm. thick. |
|---|---|---|
| 800 ... ... ... | $0\cdot26\times10^{-6}$ ... ... | $2\cdot25\times10^{-6}$ |
| 850 ... ... ... | 1·15 ... ... ... | 7·4 |
| 875 ... ... ... | 2·23 ... ... ... | 8·3 |
| 900 ... ... ... | 4·60 ... ... ... | 10·0 |
| 925 ... ... ... | 9·95 ... ... ... | 16·8 |
| 950 ... ... ... | 20·40 ... ... ... | 24·7 |

If the logarithms of the diffusion rates are plotted against the reciprocal of the absolute temperature, straight lines are obtained so that the usual diffusion law is followed. By making certain reasonable assumptions about the solubility of oxygen and carbon, the diffusivity constants can be calculated. At a temperature of 1000 deg. Cent. the value for carbon is $7\cdot2\times10^{-8}$, and for oxygen $23\cdot6\times10^{-10}$. For carbon monoxide at 1050 deg. Cent. it is $14\cdot0\times10^{-8}$. It will be noticed that the value for carbon is almost the same as that of carbon monoxide, but quite different from that of oxygen.

It is concluded from these experiments that the carbon monoxide which can be de-sorbed from nickel at high temperatures is derived from oxygen and carbon, and that the controlling factor in the rate is the diffusion of carbon from the interior of the metal to the surface. A nickel wire was completely degassed, and just visibly oxidised at a low pressure of oxygen. On heating again *in vacuo* a further evolution of carbon monoxide took place. It is difficult to understand why the rate of degassing is not controlled by the slower of the two diffusion processes involved, *i.e.*, the oxygen ; and the authors suggest that the oxygen is concentrated at or near the surface of the wire, so that the rate would be determined by the diffusion of the carbon. They were, however, unable to obtain any experimental confirmation of this. They also suggest that the diffusion of oxygen is confined to the grain boundaries whilst carbon diffuses through the lattice.

In a further communication,‡ the same authors describe some results obtained for the diffusion of oxygen and hydrogen through nickel at high pressures. They point out that diffusion probably involves three processes :—

(1) Adsorption on the surface.
(2) Penetration of the metal.
(3) Diffusion through the metal.

At low pressures adsorption on the surface would perhaps be the controlling process, but when the surface becomes completely covered the rate should be independent of P. Actually most of the experimental results show that the diffusion is proportional, except at very low pressures, to $\sqrt{P}$. The authors measured the rate of diffusion of hydrogen through nickel up to 112 atmospheres at 248 deg. and 400 deg. Cent., and also the diffusion of oxygen, which neces-

† THE METALLURGIST, 1935–36, 10, 68.

‡ "Proc.," Roy. Soc., 1936, A, 157, 292.

sitates the presence of an oxide film at higher pressures.

### DIFFUSION OF HYDROGEN THROUGH NICKEL.

The rate of diffusion was determined at various pressures from 10 to 112 atmospheres and the results showed conclusively that over this range of pressure the square root law is accurately obeyed.

### DIFFUSION OF OXYGEN THROUGH NICKEL.

The method of measuring the diffusion of oxygen was the one described previously in this review. It was found that with pressures of oxygen about 0·1 mm., the surface of the tube remained untarnished but with pressures above 0·25 mm. the surface was always covered with a visible layer of green nickel oxide. The results are given in Table IV. It will be

TABLE IV.—*Diffusion of Oxygen Through Nickel at 900 deg. Cent*

| Oxygen pressure, mm | Rate of evolution of CO, c.c./sec./cm.² for 1 mm. | D. |
|---|---|---|
| 0·0012 | 0·22 × 10⁻⁸ | 0·11 × 10⁻⁸ |
| 0·0048 | 0·62 | 0·31 |
| 0·025 | 1·32 | 0·66 |
| 0·050 | 2·27 | 1·13 |
| 0·25 | 3·69 | 1·84 |
| 0·30 | 4·07 | 2·03 |
| 0·57 | 3·92 | 1·96 |
| 3·77 | 4·60 | 2·30 |
| 112·00 | 4·13 | 2·06 |

noticed that at pressures above 0·25 mm. the rate of diffusion is constant, but below this pressure the rate falls off. In the latter range the rate seems to be proportional to the square root of the pressure.

It is significant that the diffusion of oxygen through nickel becomes independent of the pressure at a pressure above that at which a layer of nickel oxide becomes visible on the surface. Oxygen appears to be supplied to the metal from the oxide layer at a rate which is independent of the gas pressure. At lower pressures it is assumed that rate of penetration of the gas through the surface is the limiting factor, and that diffusion through the metal is relatively rapid. In this range of pressure the rate of diffusion is roughly proportional to $\sqrt{P}$, similar to the diffusion of hydrogen.

Smithells and Ransley consider the mechanism of diffusion from the standpoint of recent theories of adsorption, but in order to explain the continued effect of pressure, in the case of hydrogen, they suggest that the rate of diffusion at higher pressures depends on the impact of the molecules of the gas phase on the atoms adsorbed in the surface. Should the bombarding molecules possess sufficient energy, the adsorbed atoms might acquire sufficient energy to penetrate the surface, and the rate of diffusion will continue to be a direct function of pressure, even after the adsorbed layer of gas is built up.

The diffusion of hydrogen through nickel and iron is also the subject of a communication to the American Society for Metals, October, 1936, by W. R. Ham. On the assumption that diffusion is "chemical" in nature, they find a linear relation between log D (diffusion rate) and log P (gas pressure) with a slope of 0·5. If the metals have not been degassed or contain elements such as carbon or nitrogen in solution this slope of the isotherms is greater than 0·5 and the increase in slope appears to be nearly proportional to the amount of foreign element in the metal. As long as no phase change (crystal structure) or electronic change (magnetic) occurs in the metal a similar linear relation exists between log D and $b/T$. With nickel and iron the magnetic changes at 360 deg. and 750 deg. Cent. are clearly indicated by diffusion data. The author's general conclusion is that the isobars from hydrogen diffusion tests provide an accurate means of detecting phase or electronic changes in nickel, and that the change in slope of the isotherms may provide a means of determining small amounts of foreign elements in solution in metals.

# Iron Oxide Films.

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No. II. (*continued from April issue.*)

### COMPOSITION OF THE FILMS.

A BRIEF outline has been given[22] of the evidence which has led the author to believe that the oxide formed on polycrystalline iron when exposed to air at temperatures well below 200 deg. Cent. is $\gamma-Fe_2O_3$, and that the one obtained above this temperature is $\alpha-Fe_2O_3$, until $Fe_3O_4$ begins to appear as an underlying layer at temperatures well above 400 deg. For convenience, an indication of the evidence is included here.

The oxide formed on polycrystalline iron in air is believed to be :—(1) $\alpha-Fe_2O_3$ when produced at temperatures above 200 deg. Cent., since it is ferric oxide [see references[23] (*a*), (*b*), (*c*), (*e*), (*g*), (*h*), (*i*) below]; non-magnetic (*a*); hexagonal in structure with lattice dimensions suitable for this oxide (*c*), (*e*) until an underlying layer of $Fe_3O_4$ appears when heated at temperatures above 400 deg. (*a*), (*h*), (*i*)—this possibly accounts for the $Fe_3O_4$ found in tinted films by Smith (*d*); and (2) $\gamma-Fe_2O_3$ when formed at temperatures well below 200 deg., since it is different from the oxide formed above 200 deg. (*c*), (*e*), (*h*), (*i*); cubic in structure with a lattice dimension suitable for either $\gamma-Fe_2O_3$ or $Fe_3O_4$ (*c*), (*e*), (*f*); ferric oxide (*a*), (*f*), (*g*), (*h*), (*i*).

It can now be shown that Nelson's valuable results are completely in line with the arguments supporting the above statement. In his first report[21] (*Nature*), he mentioned only $Fe_3O_4$ in the discussion of the cubical oxide formed at temperatures below 200 deg. Recently[21] (private communication), he has made it clear that from his measurements the oxide might be either $Fe_3O_4$ or $\gamma-Fe_2O_3$. He said that in a more detailed paper[21] (*Journal of Chemical Physics*) he had pointed out that his experiments do not distinguish between $Fe_3O_4$ and $\gamma-Fe_2O_3$. It is significant that Nelson was able to change the "cubical pattern" to that characteristic of $\alpha-Fe_2O_3$ by heating the films at 200 deg.

Mehl and McCandless[22] did not report any differences in the composition of the oxide films they obtained on monocrystalline iron at temperatures below and above 200 deg. It seems reasonable to suppose that the composition of the films formed on monocrystalline iron should not be appreciably different from that of the films produced on polycrystalline iron at the same temperatures.

### COLOURS OF THE FILMS.

Vernon observed[8] that films obtained by heating polycrystalline iron in air at temperatures well below 200 deg. gave no colours other than a general darkening of the specimens, even when the amount of oxidation was sufficient to have caused colours at temperatures above 200 deg. This has been con-

firmed by the author,[1] and an explanation given elsewhere[22] for these differences in the interference effects caused by oxide films on polycrystalline iron, and also for the differences between the effects of films on monocrystalline and polycrystalline iron below 200 deg. Mehl and McCandless[22] have observed bright colours on monocrystalline iron when heated at temperatures down to 140 deg., the lowest temperature at which they worked.

Evans has shown[24] that the interference effects produced by an oxide film depends principally on (*a*) the reflection[25] at the back of the film, (*b*) its transparency, and (*c*) its uniformity. The light that enters the film will be reflected back and forth until it is absorbed or emerges in phase with the light reflected from the outside surface. Due to lack of perfection in the three factors mentioned, the light will suffer losses in the film, and the wave-lengths nearest to the interference value will be reflected the greatest number of times, and will accordingly lose more in intensity. By plotting the intensity of the emerging light against the wave-length, an absorption band is obtained with a minimum value at the interference wave-length. Either an infinitely narrow band or a very broad one will give no colours, but colours of different brightnesses will be given by bands between these limits. The bands of intermediate widths are best for producing bright colours. A collodion film may be so nearly perfect in reflection, transparency and uniformity that it will have an absorption band that is too narrow to give colours.[24] Metal oxide films are not expected to attain this standard of perfection, and their bands are generally toward the broad side of the absorption limits.

The $\alpha-Fe_2O_3$ (hexagonal structure[26]) on polycrystalline iron (*a*) is possibly crystallographically discontinuous with the metal base and has a relatively irregular inner surface, (*b*) is known to have a relatively high transparency, and (*c*) is non-uniform, and will therefore be expected to give an absorption band which is medium to broad. Constable's optical measurements[3] show bands for tinted films on iron which appear to be broad. A film of the same oxide on monocrystalline iron would have all of the optical conditions repeated except it would have a smoother and better inner reflecting surface and be much more uniform, and these differences would tend to shift the band from medium or broad in the direction of narrow. Hence the $\alpha-Fe_2O_3$ film on either kind of iron would be expected to give colours. The $\gamma-Fe_2O_3$ (cubic structure) on polycrystalline iron (cubic structure) differs from $\alpha-Fe_2O_3$ on the same iron in that it is possibly in optical continuity with the metal base, and provides poor inner reflecting conditions and has a low transparency, and accordingly it gives an absorption band that appears to be too broad to produce colours. A $\gamma-Fe_2O_3$ film on monocrystalline iron is expected to have a smoother inner reflecting surface, in addition to being more uniform, and to give a band that is not too broad for colours. Oxide films on monocrystalline iron of any composition might give colours because of the relatively great uniformity and the smoothness of the inner reflecting surface that would be expected.

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[23] The references used in this outline are:—
(*a*) U. R. Evans, *J.* Chem. Soc., 1927, p. 1020; 1930, p. 478.
(*b*) U. R. Evans and J. Stockdale, *J.* Chem. Soc., 1929, p. 2651.
(*c*) W. H. J. Vernon, "Trans.," Faraday Soc., 1935, 31, 1668.
(*d*) N. Smith, *J.* Amer. Chem. Soc., 1936, 58, 173.
(*e*) H. R. Nelson, *Nature*, 1937, 139, 30; Private Communication, 1937, March 19th; *J.* Chem. Phys., 1937, 5, 252.
(*f*) I. Iitaka, S. Miyake and T. Iimori, *Nature*, 1937, 139, 156.
(*g*) U. R. Evans and H. A. Miley, *Nature*, 1937, 139, 283.
(*h*) H. A. Miley, Iron and Steel Inst. Carnegie Scholarship Memoirs, 1936, 25, 197.
(*i*) H. A. Miley, unpublished work.

[24] U. R. Evans, *Chem. Ind. Rev.*, 1926, 4, 211; at the foot of page 212, the figures "$\lambda/2$, $3\lambda/2$, $5\lambda/2$," should read "$\lambda/4$, $3\lambda/4$, $5\lambda/4$," as pointed out by U. R. Evans, *Koll. Zeitsch.*, 1934, 69, 129.

[25] The reflection at the back of the film is dependent on two possible conditions. (1) If there is a similarity in the positions of the metal atoms in the metal lattice and in the oxide lattice, the oxide may be in optical continuity with the metal base, so that no good reflecting surface may be provided at the interface. (2) For the same lattice relationship the reflection will be affected by the degree of smoothness or regularity of the interface.

[26] It is really rhombohedral, but as this may be considered a special type of hexagonal it is generally classed as hexagonal.

# A New Alloy of the Elinvar Type.

ABOUT twenty years ago C. E. Guillaume was able to modify his well-known alloy, Invar, having a very low temperature coefficient of linear expansion, in such a way as to reduce the temperature variation of modulus of elasticity to a very small value. This led to the production of Elinvar, containing about 34 per cent. of nickel and 12 per cent. of chromium, the elastic modulus of which was almost constant over the range −75 to +75 deg. Cent. For the purpose of hair springs for watches and chronometers this property is of more importance than a low coefficient of expansion, but the alloy suffered from the defect of being too soft to be manipulated without injury, and not sufficiently brittle to be broken by a right-angle bend with the pliers which are almost universally employed by watchmakers to remove the excess of length of the hair spring. These defects were partially corrected by the addition of carbon and tungsten to the alloy. Nevertheless, and in spite of the necessity for employing bimetallic compensating balance wheels, carbon spring steels were frequently preferred. The raising of the elastic limit of Elinvar, while retaining its excellent thermal compensation, thus became a matter of considerable importance, which has been dealt with recently by Monsieur P. Chevenard and his associates.* These authors first summarised some of the difficulties encountered in the investigation. Solution and precipitation were found to have a considerable influence on the modulus/temperature curve, and unless complete precipitation accompanied reheating for hardening the alloy was liable to ageing effects. The hair spring occupies so small a volume in relation to the initial grain size of the cast alloy that heterogeneity may exert a harmful effect on the uniformity of a batch of spirals, and may even cause variation of properties along the length of one and the same hair spring. Finally, in practice, it is desirable that only one thermal operation should be applied to the spring, and that this should serve for the setting of the spring, the necessary hardening,

* P. Chevenard, L. Huguenin, X. Waché, and A. Villachon, "New Alloys of the Elinvar Type, Susceptible to Structural Hardening," *Comptes Rendus*, 1937, 204, 1231.

conferment of stability against ageing and securing of the minimum thermo-elastic coefficient. All these properties have been studied by the authors in the laboratories at Imphy; the precipitation of constituents and the appearance of heterogeneity by thermo-magnetic analysis, the hardening by micro-mechanical methods, internal friction and the thermo-elastic coefficient by the torsion pendulum, stability by the dilatometric method, and setting by a simplified relaxation test. At the same time, practical experience of the alloys was being obtained by Messieurs Defossez and Hofer.

The investigators arrived at two solutions of the problem of the hair spring of constant elastic modulus and high elastic limit :—

(1) Hardening by precipitation of carbide in alloys of the Elinvar type to which vanadium, molybdenum, or titanium had been added.

(2) Additions of aluminium and titanium (as used to obtain austenite of high strength at raised temperatures) to the Invar type of alloy.

Of these the second leads to higher elastic limits and is preferred by the authors. To take an example, an alloy with nickel 40, aluminium 2, and titanium 2 per cent., quenched before drawing, then heated for some hours between 600 deg. and 650 deg. Cent., showed an elastic limit of 87 tons per square inch, measured in a small test piece of 1·5 mm. diameter. The reheating caused the almost complete precipitation of a hard constituent containing nickel, aluminium and titanium, it assured accurate setting of the spring, and conferred on it an elastic limit equal to that of a carbon steel spring. A hair spring of this material working with an ordinary brass balance wheel gave rise, in a practical trial in a chronometer, to a thermal error of some tenths of a second only per degree per day.

## Hardening of Silicon-Aluminium Alloys.

IT has long been known that the hardness of silicon-aluminium alloys is increased by soaking at a high temperature and quenching to retain the maximum amount of silicon (1·5 per cent.) in solid solution. A low temperature heating of the quenched alloys produces a further increase in hardness owing to precipitation effects. In a recent paper W. Helling* describes the effects of increasing silicon contents and of the presence of impurities, especially iron, on the hardening phenomena. His work was carried out on aluminium alloys containing 0·1 to 11·3 per cent. silicon and 0·1 to 0·2 per cent. iron in the form of sheet 2·5 mm. thick and wires 2·5 mm. in diameter.

After annealing for three hours at 570 deg. Cent., quenching in cold water and reheating for two hours at 200 deg. Cent., the percentage increase in hardness over the quenched hardness rises sharply with increasing silicon content to a pronounced maximum of 45 per cent. with 1·5 per cent. silicon and then decreases more slowly to zero at about 6–7 per cent. silicon; alloys with 8 to 11 per cent. silicon actually show a decrease of about 5 per cent. in hardness after the low temperature reheating. These results are ascribed to an increase in the number of silicon nuclei present, so that the silicon is reprecipitated from solid solution in a less dispersed form with increasing silicon content above the limiting solid solubility at high temperature.

* *Z. Metallkunde*, 1937, 29, 25.

Since iron reduces the solid solubility of silicon in aluminium, according to V. Fuss,† it is to be expected that the hardening effects obtainable by heat treatment will decrease with increase in the iron content of the alloys. The curves obtained by reheating at 180–200 deg. Cent. alloys quenched from 540–570 deg. Cent. show this to be the case (Fig. 1). With 0·017 per cent. iron the maximum increase in hardness on reheating increases with the silicon content in a smooth curve to 100 per cent. at the limit of silicon solubility, with 0·1 per cent. iron the maximum increase in hardness is only 60 per cent., and with 0·25 per cent. iron only 50 per cent.; in the last case the maximum occurs with only 1·3 per cent. silicon. The hardening effects obtained with 0·52 per cent. iron are small and irregular; in this alloy the silicon and iron exist chiefly as a ternary compound with aluminium, the solubility of which in aluminium is practically negligible.

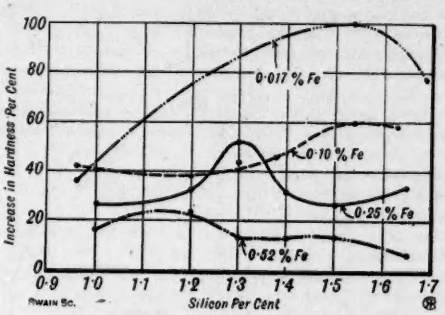



FIG. 1.—*Increase in the Brinell Hardness of Silicon-Aluminium Alloys as a Function of the Silicon and Iron Contents.*

The tensile strength of wires of the 1·54 per cent. silicon alloy is greatest when the alloys are drawn in the solid solution state, as will be seen from Table I showing the strengths developed after drawing from 4·5 to 2·5 mm. in the quenched and age-hardened states.

TABLE I.

| Heat treatment. | Tensile strength in kg. per square mm. | |
|---|---|---|
| | Before drawing. | After drawing. |
| (1) Annealed three hours at 570 deg., quenched | 12·7 | 25·2 |
| (2) As (1), reheated at 218 deg. for four minutes | 15·3 | 25·3 |
| (3) As (1), reheated at 218 deg. for sixty minutes | 19·3 | 23·2 |
| (4) As (1), reheated at 218 deg. for sixteen hours | 15·3 | 20·0 |
| (5) As (1), reheated at 320 deg. for eight hours | 11·3 | 17·3 |

Fig. 2 shows the changes which occur in tensile strength, elongation, twisting capacity, electrical conductivity, rate of dissolution in "mixed acid," and proportion of precipitated silicon during the ageing at 218 deg. Cent. of the alloy containing silicon 1·54 and iron 0·12 per cent. after quenching from 570 deg. Cent. It will be seen that the elongation and twisting capacity fall rapidly from the beginning of heating, reaching a minimum in about twenty minutes, whereas practically no change occurs in tensile strength, electrical conductivity, or rate of

† "Metallographie des Aluminiums," Berlin, 1934.

dissolution in " mixed acid " during the first minute, after which, however, all these properties increase rapidly, the rate of dissolution reaching a maximum in about the same time as the tensile strength (thirty to sixty minutes), and the electrical conductivity only after fifteen hours. Measurable precipitation of silicon occurs only after two minutes, 61 per cent. is precipitated in thirty minutes, and 81 per cent. in one hour; precipitated particles are visible under the microscope only after prolonged heating at 300 deg. Cent.

Treatment of the aged 1·5 per cent. silicon alloy in sodium chromate solution (M.B.V. process) produces an adherent light grey film provided that the period of ageing is not too long; when the alloy contains relatively coarse silicon particles a patchy darker coating is obtained which affords a much reduced protection against corrosion. Table II shows the loss in weight in grammes per square metre per day of the 1·54 : 0·12 silicon-iron alloy in various solutions after ageing for different periods at 218 deg. Cent.

The results in this table show that in no other of the solutions tested is there a sudden increase in the rate of dissolution, such as is shown in " mixed acid." In the oxidising salt test and in 0·5 per cent. caustic soda the loss in weight per day increases with increase in the precipitated silicon to a maximum, whereas this has no effect on the rate of corrosion in water vapour or acetic acid. In the Mylius test the first effect of ageing is to reduce the reactivity number from 0·55 to 0·07 (fifteen minutes at 218 deg. Cent.); further ageing results in a rapid increase in the reactivity proportional to the precipitated silicon. The behaviour with caustic soda solution varies with the concentration; in 0·5 per cent. solutions the rate of dissolution increases, but in 0·05 per cent. solutions it decreases with time of ageing and becomes very small after ageing for more than one hour, since the surface becomes covered with a protective film of finely divided silicon.

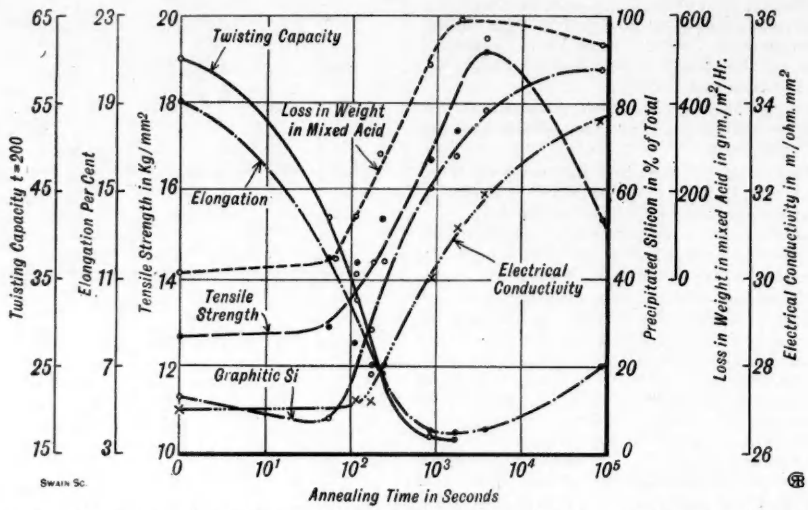



**FIG. 2**—*Changes in Properties of the 1·5 per cent. Silicon-Aluminium Alloy with 0·1 per cent. Fe on Annealing at 218 deg. Cent. after Quenching from 570 deg. Cent.*

TABLE II.—*Loss in Weight of an Aluminium Alloy with 1·54 Per Cent. Silicon and 0·12 Per Cent. Iron, Annealed at 570 Deg. Cent. for Three Hours and Quenched.*

| Time of ageing at 218 deg. Minutes. | Precipitated silicon, per cent. | Loss in weight in mixed acid, grm./m.²/hour. | Mylius number. | Loss in weight in grammes per square metre per day. | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0·5 per cent. caustic soda. | 20 per cent. sulphuric acid. | Oxidising salt solution. | Water vapour at 40 deg. Cent. | 40 per cent. acetic acid. | 0·05 per cent. caustic soda. | | |
| | | | | | | | | | Two days. | Seven days. | Sixty days. |
| — | 0 | 17·1 | 0·55 | 117 | 0·55 | 0·041 | 0·012 | 0·054 | 2·16 | 11·6 | 16·5 |
| 4 | 36 | 488 | 0·14 | 117 | 0·75 | 0·056 | 0·002 | 0·060 | 1·65 | 11·5 | 18·5 |
| 15 | 58 | 510 | 0·07 | 121 | 0·71 | 0·079 | 0·005 | 0·047 | 2·08 | 10·8 | 14·1 |
| 30 | 62 | 598 | 0·74 | 132 | 0·79 | 0·090 | 0·0007 | 0·051 | 2·2 | 11·3 | 11·3 |
| 60 | 81 | 546 | 1·50 | 170 | 0·82 | 0·095 | — | 0·062 | 1·8 | 9·1 | 0·1* |
| 24 hours | 94 | 529 | 1·85 | 186 | 0·86 | 0·110 | — | 0·064 | 1·45 | 8·7 | 0·13* |

* Increase in weight.

## The Effect of Hydrogen on Steel.

ALTHOUGH methods of estimating gases in metals have been widely developed, and much work has been done on the solubility of different gases in pure metals and on diffusion phenomena, knowledge of the influence of gases on the behaviour and properties of

metals is still relatively small. In their effects on steel, oxygen and nitrogen have received far more attention than hydrogen. Yet in melting furnaces the steel is nearly always in contact with an atmosphere which carries a varying amount of hydrogen, free or combined, derived from the moisture of the air, from the gases used in heating or from the fluxes added to the slag or other additions to the bath. From this atmosphere considerable quantities of hydrogen can get into the steel, and a desire to trace the influence of this hydrogen on the behaviour of steel through all the stages of manufacture, mechanical, and heat treatment down to its final marketable condition, has led P. Bardenheuer and E. H. Keller* to undertake the studies now published under the title "The Influence of Hydrogen, Absorbed in Melting, on Steel."

*Experimental Procedure.*—Melts of about 15 kilos. in weight were made in a high-frequency furnace. Scrap with the following composition was used for all melts:—Carbon, 0·20 per cent.; silicon, 0·29; manganese, 0·42; phosphorus, 0·012; sulphur, 0·035 per cent.; and for alloying or deoxidation the following materials were used:—Ferro-manganese, with 91 per cent. manganese; ferro-silicon, with 97 per cent. silicon; Mond nickel; ferro-chromium, with 61 per cent. chromium; 25 per cent. phosphorus-iron; and 30 per cent. sulphur-iron. Hydrogen was introduced into the liquid steel by means of a silica tube passing through a refractory cover provided with a gas outlet and luted to the crucible with asbestos packing, rapid and homogeneous distribution being achieved by the electro-dynamic motion of the liquid metal.

*The Influence of Hydrogen on the Composition of the Bath.*—The amount of the ordinary elements present in the steel is almost uninfluenced by hydrogen treatment of the bath. The analytical data given show that the content of manganese, phosphorus, and sulphur is unaffected. In two melts a small decrease in carbon content occurred, but this was accompanied by a rise in silicon, indicating that the fall in carbon content was not to be ascribed to the action of hydrogen, and that it was due to the reduction of silica (derived from the crucible) by carbon, a reaction which, according to the studies of Bardenheuer and Bottenberg† may proceed under suitable conditions. The analyses of the melts clearly showed that the hydrogen reacted with the oxygen present in the molten steel, and thus deoxidising of the steel with hydrogen is theoretically possible.

*The Influence of Hydrogen on the Casting Properties.*—Steels made with various carbon contents (0·04 to 1·20 per cent.) were deoxidised 10 min. after melting by the addition of ferro-manganese and then ferro-silicon (equivalent to 0·35 per cent. manganese and 0·15 per cent. silicon). One part of each melt was immediately cast into two or three ingots in a square chill mould (50 mm. by 50 mm. by 140 mm.). The rest was treated for 10 min. in the furnace with hydrogen and cast into similar ingots. At the same time test pieces for the study of gas content and chemical composition were cast in small thick-walled copper moulds. No alteration of chemical analysis was brought about by the hydrogen treatment. The melts not treated with hydrogen were quiet in the furnace, and also in the ladle and the mould. They gave piped ingots with a smooth surface. After the hydrogen treatment, the steel was very lively in the furnace and in the ladle. During solidification little flames of gas were ejected, the steel rose in the mould and gave an ingot whose surface was arched and uneven. Longitudinal sections through the middle of the ingots showed that they were full of cavities having a bright metallic surface, while the untreated ingots were solid. The composition of the steel appeared to be without influence. High carbon steels and alloy steels showed the same behaviour in casting as the steels of lower carbon content. The average degree of unsoundness determined by measuring the density of the ingots was 2·7 c.c. of cavities per 100 grammes of steel.

The behaviour of the hydrogen-treated steel is just as might be expected from the known facts about the solubility of hydrogen in iron, especially the marked change at the freezing point where the solubility was found by Sieverts to fall suddenly from about 27 c.c. to 13 c.c. per 100 grammes of metal. But the solubility continues to fall rapidly, after solidification, to about 5 c.c. per 100 grammes at 1000 deg. Cent., and there is the possibility that gas may continue to collect under increasing pressure in the already existing cavities. It is suggested by Bardenheuer and Keller that the pressure in a single blow-hole may become so great as to exceed the resistance of the steel at the high temperatures involved, and by overcoming the intercrystalline cohesion, to force a way out. In some ingots, cast after treatment with hydrogen, pores appearing on the outside surface were held to have been formed in this way.

*The Influence of Hydrogen on the Forging Properties.*—Small ingots of carbon, nickel, and nickel-chromium steels, both before and after the introduction of hydrogen, were forged before going cold. The hot working of the steels before hydrogen treatment presented no difficulty whatever. On the other hand, after the introduction of hydrogen the behaviour of the steels was very different. The softest steels, forged at 1100–1200 deg. Cent., shattered at the first blow. With increasing carbon content the forgeability was better. Moreover, on continuing the process of forging below 1000 deg. Cent. no more defects appeared. If the first ingot broke in forging, or showed any defects, a second ingot which had been held at 1200 deg. Cent. after casting was forged. Defects were reduced in extent even when the ingot had been held for only five minutes at this temperature. Further, if the ingots of the steel treated with hydrogen were first cooled to room temperature and then reheated they could be forged without difficulty. Every tendency to the formation of flaws seemed to have disappeared. With carbon more than 0·6 per cent. the influence of hydrogen was no longer observed.

In contrast with plain carbon and nickel steels, nickel-chromium steel with about 3·3 per cent. nickel and 1·0 per cent. chromium did not show hot-shortness after hydrogen treatment. Even when the carbon content was very low (0·06 per cent.) these alloy steels could be forged well.

*The Influence of Hydrogen on Susceptibility to Red-shortness.*—Ingots were forged, before going cold, into bars 15 mm. square. If a first ingot was hot-short, a second which was held ready at the forging temperature was forged in the same way. The bars thus produced and before going cold were notched to one-third of their thickness and bent double at a temperature of 800–900 deg. Cent. All the steels cast before hydrogen treatment were free from red-shortness. After hydrogen treatment the soft steels showed pronounced red-shortness which diminished in intensity as the carbon content increased and with

* *Mitt. K.W. Inst. Eisenforschung*, 1936, 18, 227.
† *Mitt. K.W. Inst. Eisenforschung*, 1934, 16, 93.

more than 0·6 per cent. of carbon was scarcely apparent. When the bars were cooled to room temperature and heated again to redness there was no longer any red-shortness, whatever the carbon content. Thus soft steels after hydrogen treatment tend to be both hot-short and red-short when work is applied before the steel has gone cold after casting, but not otherwise; while hydrogen has no influence on the forgeability of steels with more than 0·6 per cent. of carbon.

Low carbon 3 per cent. nickel steels and nickel-chromium steel with nickel 2·72, chromium 0·68 per cent. showed hot and red-shortness after hydrogen treatment, like carbon steels; but with higher alloy content the nickel-chromium steels which were not brittle at very high temperatures showed red-shortness on reheating to about 1000 deg. Cent.

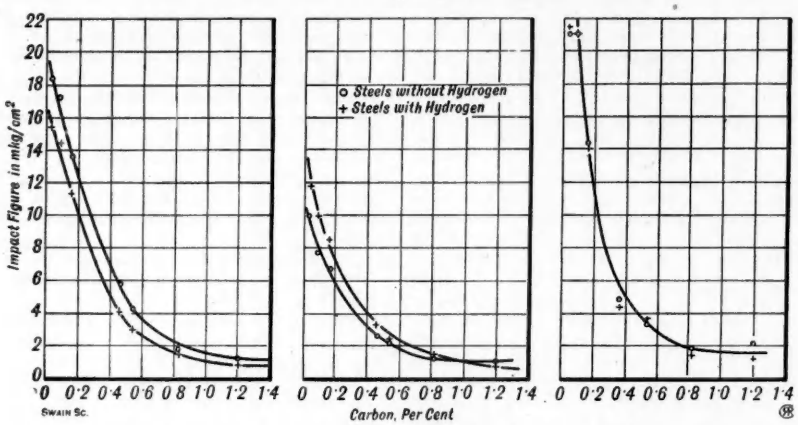
The failure of the steels in forging was attributed by Bardenheuer and Keller to the damage done by the pressure of the hydrogen eliminated as the steel cools, reinforced by the stresses imposed by the forging operation. If the steel is allowed to go cold and is then reheated and forged, the grain boundary weakness which may have been caused by the escaping gas can again be welded up by forging. If, on the other hand, the hydrogen is allowed to escape by holding the ingot at 1200 deg. Cent. before forging, the increase in internal pressure imposed by the forging operation no longer suffices to break down the material.

A short time at 1200 deg. Cent. was sufficient to improve the forging properties of these small hydrogen-treated ingots. A longer time would be required for larger ingots.

*The Influence of Hydrogen on the Tendency to Sliding Fracture.*—Transverse tests of alloy steels sometimes show a stepped or inclined fracture not accompanied by much reduction of area and referred to as a "sliding" fracture in contrast with the cup and cone fracture of more homogeneous material.

In order to study the influence of hydrogen absorbed in the melt on the occurrence of sliding fractures in nickel-chromium steels comparative tests were carried out before and after hydrogen treatment. Ingots were forged down before going cold to a bar 30 mm. square and part of this bar was further forged to a plate 10 mm. thick, which was notched longitudinally on both sides and fractured. The steel which had received no hydrogen treatment showed a uniform granular fracture. All the steels which had been treated with hydrogen showed defective fractures, and the tendency to give sliding fractures was not removed by subsequent heat treatment.

*The Hydrogen Content of Steels After Solidification and After Forging.*—Immediately after hydrogen treatment test pieces were cast in a thick-walled copper mould. It was assumed that by rapid cooling the greater part of the hydrogen would be retained in the test piece. Another ingot was cast in the usual iron mould and forged, before going cold, to a 15 mm. square bar. Measurements of hydrogen evolution were made in a special gas-collecting vessel in which the test piece was immersed in mercury and the hydrogen liberated in a given time was measured directly. The measurements were continued so long as a measurable amount of hydrogen continued to be evolved, and the remainder was estimated by the hot extraction method (Tables I and II). The rate of evolution of hydrogen in the gas receiver fell off rapidly. The amount of hydrogen corresponding to the maximum solubility determined by Sieverts after solidification (13·3 c.c. per 100 grammes) was never found, as much hydrogen was given off in the mould and gas evolution was assisted by forging. The total hydrogen content was found to increase with carbon content, either because the hydrogen does not diffuse out so well through the harder steel or, alternatively because, with increase in carbon content, more hydrogen is in the course of cooling converted into and retained as methane. The data on the cast




FIGS. 1–3.—*Influence of Hydrogen Treatment on the Impact Figure of Steels* (1) *as Forged*, (2) *compressed* 10 *per cent. and heated Two Hours at* 200 *deg. Cent.*, (3) *After Normalising.*

TABLE I.—*Chemical Composition.*

| Melt No. | C, per cent. | Mn, per cent. | Si, per cent. | P, per cent. | S, per cent. | O, per cent. |
|---|---|---|---|---|---|---|
| 33 | 0·12 | 0·24 | 0·05 | 0·021 | 0·031 | 0·023 |
| 34 | 0·38 | 0·51 | 0·15 | 0·022 | 0·030 | 0·008 |
| 35 | 0·58 | 0·30 | 0·21 | 0·023 | 0·031 | 0·010 |
| 36 | 0·71 | 0·24 | 0·01 | 0·021 | 0·030 | 0·009 |
| 37 | 0·01 | 0·01 | 0·04 | 0·028 | 0·038 | 0·073 |
| 38 | 1·90 | 0·14 | 0·07 | 0·021 | 5·280 | 0·020 |
| 39 | 0·65 | 0·41 | 0·09 | 5·210 | 0·035 | 0·012 |

specimen of melt 38 with high sulphur content confirm the hypothesis that hydrogen sulphide is formed and retained in the steel, since the steel gives out very little hydrogen in a long time under mercury and the greater part is first obtained during hot extraction. The total hydrogen influenced by the high sulphur content of the steel reaches the high value of 33·5 c.c. per 100 grammes. Melt 39 containing 5·21 per cent. of phosphorus does not show similar behaviour presumably because of the lesser stability of phosphoretted hydrogen.

After the introduction of hydrogen and before the time of casting the molten steel was giving up

TABLE II.—*Hydrogen Content of the Steels.*

| Melt No. | Type of specimen. | Time between solidification and collecting gas. | Time in gas receiver. | Hydrogen, c.c./100 g.* | | |
|---|---|---|---|---|---|---|
| | | | | Gas receiver. | Hot extraction. | Total hydrogen content. |
| | | Min. | Hours. | | | |
| 33 | Cast ... | 12 | 354 | 4·58 | 3·17 | 7·75 |
| 34 | | 15 | 234 | 6·61 | 3·39 | 10·00 |
| 37 | | 8 | 406 | 2·83 | 4·71 | 7·54 |
| 38 | | 11 | 721 | 3·80 | 29·70 | 33·50 |
| 39 | | 11 | 632 | 6·84 | 5·50 | 12·34 |
| 33 | Forged | 13 | 354 | 2·73 | 2·50 | 5·23 |
| 34 | | 20 | 235 | 3·02 | 2·72 | 5·74 |
| 35 | | 13 | 819 | 3·35 | n.d. | 3·35 |

* Average of two or three estimations.

hydrogen owing to the removal of the hydrogen atmosphere from over the bath. The rate at which this occurred was measured in melts 35 and 36 (Tables I and III). Both were treated with hydrogen for ten minutes and then kept liquid, specimens being

TABLE III.—*Hydrogen Evolution from Liquid Steel.*

| Melt No. | Time of sampling after treatment. | Hydrogen, c.c./100 g. | | |
|---|---|---|---|---|
| | | Gas receiver. | Hot extraction. | Total hydrogen content. |
| 35 | Immediately ... | 3·63 | 2·37 | 6·00 |
| | 15 min. ... ... | 3·00 | 1·26 | 4·26 |
| 36 | Immediately ... | 2·54 | 5·35 | 7·89 |
| | 15 min. ... ... | 1·81 | 4·05 | 5·89 |
| | 30 min. ... ... | 1·26 | 4·07 | 5·33 |
| | 45 min. ... ... | 1·05 | 2·28 | 3·33 |

cast at intervals in thick-walled copper moulds and placed immediately after cooling in the gas collecting vessel. In melt 35 slag was left on the surface, but all slag was removed from melt 36. The hydrogen was slowly given up by the liquid bath, but considerable amounts still remained in the solid cast some time after the completion of the hydrogen treatment.

*The Influence of Hydrogen on the Impact Value and on the Susceptibility to Ageing of Plain Carbon Steels.*—The effect of hydrogen treatment on impact figure and susceptibility to ageing was determined in a series of carbon steels treated as before with hydrogen for ten minutes. Ingots were cast before and after treatment and forged before going cold to 15 mm. diameter bar. Hardness and impact tests were made in the forged condition, another set of tests after compressing 10 per cent. and heating for two hours at 200 deg. Cent., and a third set after normalising. The results of these impact tests are given in Figs. 1 to 3 and show that the hydrogen-treated steels have the lower initial impact figure, but after identical ageing treatment do not show so great a fall in impact value as the hydrogen-free steels. Both sets give similar figures after normalising.

*Conclusions.*—The paper by Bardenheuer and Keller serves again to direct attention to the important part which hydrogen derived from furnace atmospheres can play in determining the properties of steel products. By the introduction of hydrogen into molten steel the carbon, sulphur, and phosphorus contents are not affected, but a reaction takes place with the oxygen present, indicating that in principle deoxidation of steel with hydrogen would be possible, though it would entail serious complications.

If an ingot of steel containing hydrogen is worked immediately after casting hot-shortness is invariably observed, but if the ingot is soaked at a temperature of about 1200 deg. Cent. the hot-shortness disappears. Red-shortness (at temperatures of 800–900 deg. Cent.) is general in hydrogen-bearing steels with less than 0·6 per cent. of carbon. Carbon steels with carbon over 0·6 per cent. do not show the initial hot-shortness after hydrogen treatment, and neither does low-carbon nickel-chromium steel with 3 per cent. of nickel and 1 per cent. of chromium, although it shows the red-shortness usual in low-carbon steels containing hydrogen. A sliding fracture is characteristic of transverse tests on alloy steels containing hydrogen, and the notched bar value of hydrogen-bearing carbon steels is reduced, but susceptibility to further reduction by ageing after cold work is diminished and the impact figure after normalising is restored to the value for hydrogen-free steel.

## The Alloys of Iron and Nickel.

IT was solely as a result of laboratory investigations that the industrial possibilities of alloys belonging to the system iron-nickel became apparent, and it is therefore not surprising that no other system is at present receiving the detailed consideration which is being given to these alloys. Notable amongst recent publications on this subject are Dr. Desch's summary of the literature and outline of the work being undertaken at the National Physical Laboratory for the Alloy Steels Research Committee[1] and papers by Owen and Yates [2, 3], Bradley, Jay and Taylor[4], and Mehl and Derge[5]. The papers indicated in references [2–4] describe X-ray investigations covering the whole system, whilst Mehl and Derge are concerned only with the iron-rich alloys in which they study the mechanism of the $\gamma \rightarrow \alpha$ transformation from a crystallographic standpoint, the paper forming a part (No. 8) of Mehl's extensive research into Widmanstätten structures.

Owen and Yates are interested primarily in the thermal expansion of the alloys, but employ X-ray measurements of the lattice constant to determine this property, as the definition of the reflections affords an accurate check that specimens are free from strain and are in equilibrium, points which are not easily verified when direct measurements of length are made on polycrystalline material. Moreover, smaller quantities of material may be used, and this becomes important when high purity alloys are under investigation. Owen and Yates used alloys prepared by Dr. Pfeil of the Mond Nickel Company; their measurements extend over the range 0–600 deg. Cent. The first paper describes the study of five alloys

containing 73 to 97 per cent. nickel (atomic). Measurements were made on powders from well annealed lump material annealed in vacuo at temperatures between 300 deg. and 800 deg. Cent. and cooled slowly. The results confirm the substitutional nature of the γ phase and indicate that when iron is added to nickel the face-centred cubic lattice of nickel expands approximately proportionately to the iron content and at the same time the temperature at which the thermal expansion curve exhibits a discontinuity is raised, though not proportionately to the iron content. This discontinuity corresponds to the magnetic transformation and is found at 370 deg. Cent. in substantially pure nickel and at 490 degs. Cent. in the alloy containing 9 per cent. iron. In this alloy the coefficient of expansion is found to increase gradually from 12·7 at 0 deg. Cent. to 17·7 at 400 deg. Cent. and 20·0 at 490 deg. Cent., after which it assumes a steady value of 16·4 (all values $\times 10^{-6}$). A similar type of curve is followed by the other nickel-rich alloys. No effect of the transformation on the lattice type has been found, but it is possible that minor changes occur in the distribution on the lattice points of the two sorts of atom, though this is rather unlikely as the same dimensional change at the magnetic transformation point is encountered in pure nickel, in which there can be no question of any "ordering." Owen and Yates summarise the situation by stating that they consider that "at a certain temperature the thermal agitation of the atoms is sufficient to release the nickel atom from the binding forces which keep it in position, and that above this temperature it may take up any random orientation."

In the second paper, Owen and Yates describe their experiments upon three alloys of higher iron content, with 41·7, 31·1, and 23·3 atomic per cent. nickel. Of these the first two lie on either side of the well-known alloy, "Invar," which has virtually a zero coefficient of expansion at ordinary temperatures, and are just within the γ range. The other alloy lies in the duplex field when in equilibrium at room temperature, and belongs to the class of "irreversible" alloys, which do not return, after a cycle of heating and cooling, to their original dimensions. The alloys containing 42·7 and 32·2 per cent. nickel yielded, when examined as annealed and slowly cooled powders, curves of lattice constant against temperature, which show that the coefficient of expansion has a low value at ordinary temperatures, but later rises gradually to a considerably higher value, which then remains practically constant on further rise of temperature. For the first alloy a coefficient of $4{\cdot}7\times10^{-6}$ is obtained up to 200 deg. Cent. and a stable value of $15{\cdot}1\times10^{-6}$ reached at 600 deg. Cent. The temperature of the transition, which again indicates the magnetic transformation, rises in this region with increase in nickel content; the early measurements of Chevenard[6] on the alloy containing 35·4 per cent. nickel (Invar) showing a transition temperature intermediate between the alloys now described. It is clear that the iron-nickel alloys in the γ phase region suffer pronounced changes on passing through the magnetic transformation, but that there is a radical difference in their behaviour according to whether they are rich in iron or in nickel, which may point to a real distinction in the atomic rearrangement, if any, involved. Owen and Yates are of the opinion that this transformation, although involving no change of lattice type, is of sufficient magnitude to be represented on the equilibrium diagram, and compare it with the $\beta\rightarrow\beta^1$ transformation in brass.

The results obtained for the alloy containing 23·3 per cent. nickel provide an explanation of the dilatometric curves given by the "irreversible" alloys, bars of which expand on heating up to a certain temperature and then contract over a range of temperature before expanding again on being further heated; when cooled a steady contraction only is observed. The X-ray measurements indicate that in the 23·3 per cent. nickel alloy both the α and γ phases have normal practically linear expansion curves and that the anomalous contraction is due to the disappearance of the body-centred α phase, which has a greater mean atomic volume than the γ phase at the same temperature. On cooling, the α phase does not reform at the temperature of the transition on heating, with normal rates of cooling, and the characteristic curve of the γ phase is traced. The extent of the hysteresis involved in the $\gamma\rightarrow\alpha$ transformation is indicated by the difficulties encountered by the authors in securing well-defined X-ray reflections from this alloy; for example, a specimen photographed after cooling from 632 deg. Cent. to room temperature showed neither α nor γ phase lines.

The work of Bradley, Jay and Taylor[4] includes the determination of the lattice spacings at room temperature of thirty-five alloys in the slowly cooled condition. The lattice constant of the γ phase is found to increase from 3·5169 for pure nickel to a maximum of 3·5878 Å at 38·69 per cent. nickel and then fall to 3·5741 at 28 per cent. nickel, which is the minimum nickel content of the γ phase in the slowly cooled alloys. These workers had reason to suspect an anomalous change in parameter in the neighbourhood of 78 per cent. nickel—the "permalloy" composition—not revealed by the previous examination of Jette and Foote[7], who stated that the change in parameter from nickel to the alloy containing 43 per cent. nickel was a linear function of the iron content. It is now found that the values obtained lie closely on two straight lines intersecting at a small angle near 78 per cent. nickel. The writer has examined the data of Owen and Yates (averages of values given at temperatures of 10–20 deg. Cent.) and has found that these lie very closely on the lines indicated by Bradley, Jay and Taylor and are not adequately represented by the formula of Jette and Foote. The γ solid solution of iron in nickel thus exhibits an extremely complex mode of dependence of lattice spacing on composition at ordinary temperatures, which departs markedly from the simple relation of Vegard.

Attention is also drawn by Bradley, Jay and Taylor to another anomaly found in the slowly cooled alloys at the iron-end of the system, where the parameter of the body-centred cubic α phase is increased from 2·8605 to 2·8644 Å for 5·7 per cent. nickel, but alloys lying in the duplex field contain α with a parameter of only 2·8635 Å, corresponding to a nickel content of about 4 per cent. The authors suppose that the transformation of the alloys containing more than 5·7 per cent. nickel is more sluggish than that of the alloys of lower nickel content and is thus checked at a higher temperature. This observation if correct illustrates the impossibility of constructing a "non-equilibrium" phase-diagram, since different alloys do not contain after a standard treatment the same phases. The further studies of Owen and Yates[13, 14, 15] indicate, however, that the parameters of the α phase pass through a maximum value (near 2·8636 Å) and then fall away to 2·8630 Å so that low values of the α phase parameter in the duplex alloys may point to high not low nickel con-

tents. There is clearly room for much further study of this section of the system. Bradley and his colleagues also found that the α phase lines in the single-phase region are very sharp, but become increasingly diffuse as the duplex field is crossed. It is suggested that beyond 11 per cent. nickel the individual particles of the two phases are probably of colloidal dimensions. When the alloys in this region were plunged into liquid air they were never completely transformed to the α phase, as suggested by Andrews,[8] but showed diffuse lines of the two phases. An alloy containing 28·9 per cent. nickel became duplex as a result of this treatment, the α lines predominating, though at room temperature it was in the homogeneous γ region. No detailed results are given for these alloys.

The face-centred cubic alloys were also examined after quenching from 700 deg., 800 deg., and 900 deg. Cent. The resulting lattice parameter values are not completely reproducible, but are, on the whole, considerably greater than those of the slowly cooled alloys. The authors draw attention to a change in parameter, in that case a decrease, found in the alloy $Ni_3Al$ as a result of quenching from above, rather than slow cooling through, the Curie point, and think that the present results are also connected with the magnetic behaviour of the alloys.

Mehl and Derge[5] have carried out a crystallographic examination of a portion of meteorite and a number of synthetic nickel-iron alloys with a view to ascertaining the mechanism by which the α phase is rejected from the γ solid solution, on cooling or during isothermal exposure at temperatures below the critical point. As these authors observe, crystallographic studies are of less practical importance than determinations of critical temperatures, rates of transformation, or concomitant property changes, but afford an opportunity of tracing the basic atomic movements which is not to be neglected.

The earlier studies of Kurdjumow and Sachs[9] had indicated the mode of breakdown of a solution of carbon in γ-iron to be such that (111) planes of the γ phase are parallel to (110) planes of the α phase with the (110) direction in the γ phase parallel to the (111) direction in the α phase. The work of Nishiyama,[10] on the other hand, had shown a different mechanism in a 30 per cent. nickel-iron alloy. Here the product of decomposition at liquid air temperatures was an arrangement with the same planes parallel, but in the (211)—gamma—and (110)—alpha—directions. Wassermann,[11] who repeated both experiments and confirmed the results, and also Dehlinger,[12] had suggested that the difference was due to the fact that carbon was dissolved interstitially in γ-iron whilst the iron-nickel solution is substitutional.

The present investigation, however, suggests rather definitely that both types of orientation can occur in duplex iron-nickel alloys depending on the temperature at which the transformation proceeds. In a meteorite containing 7 per cent. nickel which was presumed to have cooled very slowly from the stable γ range and thus transformed at a fairly high temperature, the relationship of Kurdjumow and Sachs seems to hold, as three (110) alpha poles lie near the (111) gamma pole in the stereographic triangle as is required by this mechanism, whereas only two are indicated by the Nishiyama mechanism. Although three definite clusters appear, there is a wide scatter in the orientation of individual α crystals, pointing perhaps to a marked lack of perfection in the structure. This tendency was also shown by measurements of the angles of a set of twenty-three "parallel" α plates in an area of 100 square inches on the plane of polish; a scatter of 3·6 deg. was observed. The individual α crystals were of a high degree of perfection as indicated by back-reflection X-ray photograms. The orientation data referred to above were obtained by the Laue back-reflection method from an area 1¼in. square.

A study was then made of a series of alloys containing 27, 28, 28·5, 31·4, and 34 per cent. nickel by weight. All but the fourth alloy were made from materials of high purity reduced in hydrogen; all the alloys were brought to a suitably coarse γ grain size by prolonged annealing at 1400 deg. Cent. It was found that only the materials containing more than 28·5 per cent. nickel could be retained in the γ condition at room temperature by quenching, and that separation of the α phase occurred in the 31 per cent. alloy at −70 deg. Cent. and in the 34 per cent. alloy at −195 deg. Cent.; alloys containing higher nickel contents are said not to be transformed in reasonable times at any temperature. This is in accordance with the indications of Bradley (see above). When the 27 per cent. alloy was furnace cooled to room temperature an extremely good Widmanstätten pattern was produced in which the individual lamellæ are distinguishable without magnification. This is probably, as the authors suggest, the best such pattern yet produced artificially in iron-nickel alloys. In this material and in the 31 per cent. alloy transformed by heating six days at 240 deg. Cent. the orientation of the phases is closely in accordance with that of the meteorite, and the mechanism of Kurdjumow and Sachs.

When the 31 per cent. alloy was treated by dipping in carbon-monoxide-acetone mixture at −70 deg. Cent. or liquid nitrogen at −195 deg. Cent. sufficiently coarse α crystals form to give sharp X-ray reflections. After the nitrogen treatment the stereographic plot is quite unlike those obtained at temperatures above normal and clearly favours the Nishiyama mechanism, although some predicted orientations were not found. The microstructure also differs from those previously described, consisting of characteristic martensite. In the specimen treated at −70 deg. Cent. the orientations afford a stereographic plot from which it is quite impossible to choose between the two suggested mechanisms, and which the authors believe to indicate that both are here applying simultaneously. These conclusions were amply confirmed by examination of other of the alloys subjected to low-temperature treatment.

We have, then, in these alloys, both types of transformation, the Kurdjumow and Sachs type here yielding well-developed Widmanstätten structures and the Nishiyama type at lower temperatures producing quasi-martensite. In carbon-iron alloys, on the other hand, martensite is the product of the Kurdjumow and Sachs mechanism, so that there does not seem much ground for Mehl and Derge's speculation that the Nishiyama transformation may always be found to follow the other on falling temperature, so that the Bain "S-curve" for the isothermal decomposition of austenite has in reality an additional lower loop. It is, of course, unquestionable that in the nickel-iron alloys such a "S-curve" diagram also relates the transformation times and temperatures, the reaction proceeding rapidly both at temperatures around 200 deg. Cent. and well below room temperature, but there seems no clear reason to identify the lower loop in the former case with the higher loop in the latter because of orientational

resemblances in their products. The Kurdjumow and Sachs relation demands for its execution primary shear in the (110) direction, *i.e.*, ordinary slip, whilst the Nishiyama mechanism involves shear in the (211) direction, *i.e.*, twinning. Slip and twinning are found from practical experience to be favoured at higher and lower temperatures respectively, so that, as the authors suggest, the mechanism which applies under given conditions may simply be that requiring the lower stress.

The group of papers under review has clarified considerably the position of the iron-nickel alloys, showing how the effect of the magnetic transformation varies with composition, indicating that the γ-phase alloys must be considered as three groups rather than one continuous series, suggesting that the behaviour of "permalloy" is a feature of the lattice, defining closely the range of the alloys in which the α-phase separates at lower temperatures, explaining the dimensional anomaly of the "irreversible" alloys in this area and describing the two mechanisms by which the γ→α transformation may proceed at appropriate temperatures.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# The Use of Polarised Light in the Microscopical Examination of Iron and Steel.

By J. H. G. MONYPENNY, F. Inst. P.

No. I.

UNTIL recently polarised light was rarely applied to the examination of metal specimens, although, of course, it has been used for many years in the study of thin sections of rocks and minerals, and has given results of the utmost value. From time to time, however, and more particularly during the last five or six years, efforts have been made by various investigators to apply polarised light to metallography, and thus provide a further means of identifying different structural components. As might be expected, however, in the development of what is practically a new branch of science, the results obtained by the earlier investigators were not always in agreement, although it was obvious that polarised light provided an effective means of distinguishing between different non-metallic inclusions, and, on that account alone, its indications were well worth close study. This particular application of polarised light in metallography has formed the major part of an extensive investigation by Schafmeister and Moll, the results of which have recently been published in Germany.[1] Their thesis presents many interesting features, and will repay careful study.

They commence by reviewing the physical basis for structural investigations with polarised light, and the methods of using it in metallographic studies. As the use of polarised light in mineralogical microscopy is well known, there is no need to devote attention to this part of the paper, beyond mentioning that the principal application of such light depends on the fact that it affords a means of distinguishing between optically isotropic and optically anisotropic bodies, as the former are single refracting and the latter double refracting. Further, optical isotropy is a function of structure, and is possessed by amorphous bodies and those which crystallise in the cubic system; all other crystals are anisotropic. Anisotropy may also be produced in isotropic bodies subjected to stress.

As regards metallography, attention has been given largely to non-metallic inclusions, as these are frequently transparent or translucent, and hence may produce appreciable effects on an incident beam of polarised light, which passes through them and is reflected back again by the metal behind them. As the authors point out, however, similar polarisation effects may be produced by opaque anisotropic bodies, *e.g.*, metals, because light penetrates to a certain depth in the metal surface, although the amplitude of vibration of the light waves diminishes very rapidly, with the result that the effects produced on polarised light are much weaker than is the case with transparent inclusions.

The authors also add a word of caution regarding

TABLE I.—*Classification of the Structural Constituents of Iron and Steel from the Point of View of their Identification in Polarised Light.*

| Material. | Composition. | Crystal structure. |
|---|---|---|
| *(a) Non-metallic inclusions :* | | |
| Silicates | $(FeO, MnO)_n SiO_2$ | Hexagonal, triclinic |
| Manganese sulphide | MnS | Cubic |
| Iron sulphide | FeS | Hexagonal |
| Cobalt sulphide | CoS | ,, |
| Nickel sulphide | NiS | ,, |
| Molybdenum sulphide | $MoS_2$ | ,, |
| Chromium sulphide | CrS | Unknown |
| Alumina | $Al_2O_3$ | Hexagonal |
| Chromite | $FeO, Cr_2O_3$ | Cubic |
| Ferrous oxide | FeO | ,, |
| Ferric oxide | $Fe_2O_3$ | Hexagonal |
| Magnetite | $Fe_3O_4$ | Cubic |
| Beryllium oxide | BeO | Hexagonal |
| Aluminium nitride | AlN | ,, |
| Iron nitride | $Fe_4N$ | Cubic |
| | $Fe_2N$ | Hexagonal |
| Titanium nitride | TiN | Cubic |
| Zirconium nitride | ZrN | ,, |
| *(b) Metallic phases :* | | |
| Graphite | C | Hexagonal |
| Cementite | $Fe_3C$ | Rhombic |
| Chromium carbide | $Cr_4C$ | Cubic |
| | $Cr_7C_3$ | Trigonal |
| Tungsten carbides | WC, $W_2C$ | Hexagonal |
| Titanium carbide | TiC | Cubic |
| Vanadium carbide | $V_4C_3$ | ? cubic |
| Iron silicide | $FeSi_2$ | Tetragonal |
| Intermetallic compound in the Fe-Cr system | FeCr | Not definitely known |
| Martensite | — | Cubic and tetragonal |
| ε-phase in the Fe-Mn system | Solid solution | Hexagonal |
| Cobalt | α-cobalt | Hexagonal |
| *(c) Metallic coatings :* | | |
| Cadmium | Cd | Hexagonal |
| Tin | Sn | ,, |
| Zinc | Zn | ,, |

[1] "Die Verwendbarkeit polarisierten Lichtes bei der Gefügeuntersuchung von Eisen und Stahl," P. Schafmeister and G. Moll. *Archiv. f.d. Eisenhüttenwesen*, 1936/37 (Oct., 1936), 155–160.

the preparation of metal surfaces for microscopic examination in polarised light. Polishing must be done very carefully, as scratches light up very strongly. Distorted surface layers are to be avoided, as they may not show the orientation of the underlying crystal. Etching is not helpful as a rule, as the surface roughness thereby produced is disturbing, owing to scattered light.

The authors give many examples of the actual use of polarised light in the examination of iron and steel, and these are worth considering in detail. They point out that iron being cubic, the usefulness of polarised light lies chiefly in identifying non-cubic constituents, which they group in three categories :—

(*a*) Non-metallic inclusions.
(*b*) Non-cubic structural constituents.
(*c*) Protective coatings of non-cubic metals.

They summarise in Table I various inclusions, constituents and metals which might be present in these three categories, with details of their composition and crystal structure.

In addition, there is also the possibility that under the influence of stress, iron might become sufficiently anisotropic to produce visible polarisation effects.

Their observations were made with a Zeiss "Neophot" microscope fitted with a swing-out polariser and a rotatable analyser. In addition, they frequently inserted a gypsum plate (first order red), as the colours thereby produced in the field of view enabled them in some cases to distinguish more easily the polarisation effects produced.

### NON-METALLIC INCLUSIONS.

Iron and manganese silicates show distinct double refraction. With ordinary light they have a dark grey to black colour, and are frequently not distinguishable from inclusions of chromite ($FeO, Cr_2O_3$). As the latter are cubic, however, identification is easy in polarised light. Between crossed nicols the particles of chromite remain dark when the sample is rotated, whereas the silicate particles become alternately light and dark four times on turning through 360 deg. The authors show a good example of this in photographs of complex inclusions in an austenitic stainless steel of the "18–8" type. Incidentally, this steel is also stated to contain inclusions of manganese sulphide which, being cubic, behave similarly to those of chromite; generally, the sulphide inclusions in such steels consist mainly of chromium sulphide, unless the manganese content of the steel is fairly high, *e.g.*, above 0·5 per cent. or so.

In cast steel silicate inclusions are spherical. They solidify in the vitreous form and are normally in a state of internal stress. When examined between crossed nicols, such inclusions light up and show an "extinction cross," as was described some time ago by Hoyt and Scheil.[2] When the sample is rotated the brightness of the inclusion does not alter, nor does the "extinction cross" rotate with the sample. The authors show examples of such silicates in a sample of remelted Armco iron, containing 0·04 per cent. Si and about 0·05 per cent. O, and mention that similar vitreous silicates, producing similar optical effects, were observed in cast steel and in ferro-chrome.

After rolling or forging, silicates are no longer vitreous. They become crystalline and under crossed nicols exhibit anisotropy, by which they can easily be distinguished from the vitreous form. In order to determine whether the latter would become crystalline on annealing, but without being worked, the Armco iron sample mentioned above was annealed in vacuo for two hours at 1200 deg. Cent., and then for eight hours at 850 deg. Cent. The inclusions, however, still showed the "extinction cross" after annealing, in the same manner as before. Hence, examination of silicate inclusions affords a means in many cases of distinguishing between the cast and the forged or rolled conditions. It may be noted that Hoyt and Scheil[3] distinguished between vitreous and crystalline silicates in a similar manner. They also pointed out that the vitreous type were occasionally contaminated with other oxides or compounds which reduced their clear transparency to a milkiness. Such "milky" inclusions were often bright under crossed nicols, but did not show the dark optical cross which is a feature of the transparent type.

As regards sulphides, the authors state that practically only manganese sulphide occurs in commercial irons and steels, this being the only sulphide which is formed in the presence of manganese, even if other alloy additions are present in greater quantity. While one would agree in a general way with this statement, it would not appear to be strictly correct in all cases. In the high chromium stainless steels, as has already been mentioned, it is probable that sulphur exists mainly as chromium sulphide unless the steels contain well over 0·5 per cent. manganese—and frequently they do not. Those who have endeavoured to take "sulphur prints" from such steels containing, for example, 0·2 or 0·3 per cent. manganese, will know that the sulphide is not appreciably attacked by dilute sulphuric acid. In the same way, the presence of even small amounts of molybdenum in steel affects considerably the determination of sulphur by the evolution method, suggesting the presence of at least some molybdenum sulphide, probably in solution in the manganese sulphide.

Manganese sulphide inclusions, when examined in polarised light between crossed nicols, remain dark at all settings on account of their cubic structure, and in this way are easily distinguishable from other sulphides, *e.g.*, iron sulphide, which can occur in steels with high sulphur and low manganese contents.

Samples containing the non-cubic sulphides of iron, cobalt, nickel, and molybdenum were prepared by melting electrolytic iron with 5 per cent. of the alloying metal and adding 0·5 per cent. sulphur. To deoxidise the melt, 0·1 per cent. aluminium was added before the sulphur addition. The sulphides were arranged in network fashion and in ordinary light had a yellow grey to brown colour. In polarised light, between crossed nicols, they were all strongly double refracting, as a result of their hexagonal structure. An attempt to produce zirconium sulphide in the same way was unsuccessful owing to the failure of the crucible used for melting.

In an oxygen-enriched melt of electrolytic iron (about 0·05 per cent. O), containing also 0·1 per cent. sulphur, the particles of the hexagonal sulphide, present in the FeS-FeO eutectic, could be distinguished easily from the cubic oxide, on examination between crossed nicols, owing to the anisotropy of the former.

Melts with high chromium and sulphur contents prepared in the same fashion contained globular and not cellular sulphide. Between crossed nicols, the larger particles, which constituted the greater proportion of the inclusions, were isotropic, whereas the smaller number of fine particles behaved anisotropically. As only iron and chromium sulphides could be present, it was concluded that the fine

[2] "Trans.," Amer. Inst. Min. and Met. Eng., 1935, 116, 405.

[3] *Loc. cit.*

particles were iron sulphide and the more numerous and larger isotropic inclusions were chromium sulphide, which, therefore, must crystallise in the cubic system. As mentioned in Table I, the crystal form of chromium sulphide has not yet been determined. When examined in ordinary light, both types of inclusions had a light grey colour and were not distinguishable. It is suggested that the finer particles of iron sulphide, which would normally be yellowish brown, perhaps contained some chromium sulphide which altered their colour.

The authors point out that samples containing inclusions of alumina are difficult to polish because the latter, being very brittle, are easily torn out, producing comet-tailed scratches. They examined a forged steel containing 2·5 per cent. aluminium and found that the inclusions, which were dirty grey in colour in ordinary light and were arranged in strings, lit up with crossed nicols but showed no difference in brightness when the sample was rotated. This abnormality in behaviour was also noted by Hoyt and Scheil[4] and is considered by the authors to be due to scattered reflection of light at the places where minute particles had been torn out from the inclusions, which themselves were very small. Owing to this scattered light producing a general illumination of the particles, the latter did not undergo extinction, when rotated, as should have occurred from their hexagonal structure.

According to Baeyertz,[5] there are two kinds of chromium oxide which can be distinguished in reflected polarised light by their red and green colours. The green phase should be pure chromic oxide, the red should contain ferric oxide as well. Oxide inclusions, of a grey to grey-black colour, were found by the authors in chrome steels, ferro-chrome and melted chromium metal; when examined in polarised light these did not show the colouring mentioned above, but, on the contrary, were isotropic. The authors conclude, therefore, that these inclusions could not be chromic oxide ($Cr_2O_3$), which is hexagonal, but were the cubic oxide, chromite, $FeOCr_2O_3$, thus confirming the observations of Urban and Chipman.[6] As further proof the authors mention that these chromite inclusions were unattacked by all the etching fluids they tried, including the one proposed by Baeyertz (1 gr. of potassium permanganate in 100 c.c. of 10 per cent. sulphuric acid), and stated by the latter to attack the green oxide. It is well to remember, however, that Portevin and Castro[7] have identified two types of crystalline oxide inclusions in chromium steels and ferro-chromes and found they have properties as described by Baeyertz, so that Schafmeister and Moll's observations may need amplification.

The authors record observations on ferrous oxide inclusions in a sample of Armco iron and also in melted electrolytic iron containing about 0·05 per cent. oxygen. These inclusions were spherical and light grey and, when examined between crossed nicols, remained dark in all positions during rotation; they were therefore cubic and were identified as ferrous oxide by etching with a concentrated alcoholic solution of stannous chloride, as proposed by Campbell and Comstock.[8] From these observations they conclude that the oxide inclusions examined by Ahmad[9] and found to be double refracting, showing a red colour between crossed nicols, could not have been ferrous oxide, as he supposed.

Ferric oxide and magnetic oxide were examined in a sample of forge scale on mild steel. The outer layer of ferric oxide was double refracting, whereas the inner layer was isotropic and hence believed to be $Fe_3O_4$. One cannot judge from the photograph which Schafmeister and Moll give whether an innermost layer of FeO was also present, nor do these authors make any mention of it.

One other type of oxide inclusion, found in low-carbon steel containing 4·7 per cent. beryllium, is described. This occurred as very small, light, angular particles which showed double refraction. It is assumed that they were beryllium oxide, which is hexagonal.

The authors also record observations of nitrides, which, they state, though unusual as inclusions in iron and steel, may be produced, for example, in electric weld metal, or by annealing either at medium temperatures in a current of ammonia or at high temperatures in air or nitrogen.

By annealing a heat-resisting steel containing 20–30 per cent. chromium and 5 per cent. aluminium in air or nitrogen for a long period at high temperatures, crystalline inclusions, of a transparent grey colour, were formed. They were identified chemically as aluminium nitride and in polarised light showed strong double refraction. The authors show photomicrographs of these and mention that the crystals, which appear, in the black and white photographs, to shine brightly between crossed nicols, actually exhibit a gorgeous play of colours like mother of pearl. When examined in ordinary light these inclusions resemble chromite in many ways, although they are easily distinguished with polarised light. The authors suggest that the anisotropic inclusions which Hoyt and Scheil[10] found in a well annealed FeCrAl alloy were probably aluminium nitride and not a complex oxide as these investigators suggested.

By nitriding mild steel the higher nitride $Fe_2N$, which is hexagonal, was formed as a fine-grained surface layer; beneath this the lower nitride $Fe_4N$, which has a cubic structure, occurred in broad bands which followed the grain boundaries of the steel. When examined in polarised light the lower nitride behaved isotropically in accordance with its structure; the higher nitride band lit up between crossed nicols, but its brightness did not vary when the sample was rotated; probably as a result—the authors remark—of the fineness of its crystalline structure.

Samples of steel containing about 1·2 per cent. chromium and 1 per cent. aluminium, after nitriding, were frequently found to have a thin surface layer which appeared bright in ordinary light, and, when examined in polarised light, was isotropic. For this reason, and also because on analysis it was found to contain 5–6 per cent. nitrogen, the authors consider it was $Fe_4N$ (which contains 5·9 per cent. N). Needles of nitride are frequently observed in sections through electrically deposited weld metal; as such needles could not be seen, without etching, on examination in polarised light, the authors conclude they also consist of the lower nitride, $Fe_4N$.

Well-formed angular inclusions of titanium and zirconium nitrides, coloured rose and pale yellow respectively, were found in steels containing these metals. Both nitrides remained dark between crossed nicols, corresponding to their cubic structure.

*(To be continued.)*

[4] *Loc. cit.*
[5] "Trans.," Amer. Soc. Met., 1934, 22, 625–634.
[6] "Trans.," Amer. Soc. Met., 1935, 33, 93.
[7] *J.*, I.S.I., 1936 (2), 213 p.
[8] "Proc.," A.S.T.M., 1923, 521.
[9] "Forschungsarbeiten über Metallkunde und Röntgenmetallographie," N. Ahmad, 1934.
[10] *Loc. cit.*